Energy, Mines and Resources Canada | Énergie, Mines et Ressources Canada

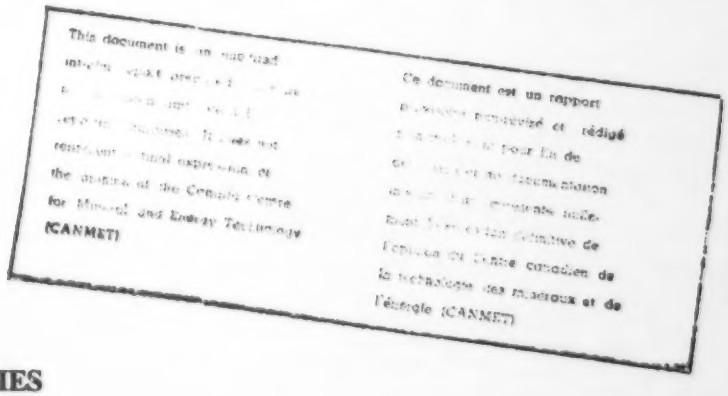
CANMET
Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

# GRAPHIC GALENA-CLAUSTHALITE SOLID SOLUTIONS IN LOW-Fe SPHALERITE FROM THE TROUT LAKE MASSIVE SULFIDE ORES, FLIN FLON, MANITOBA

**R.E. Healy**
**Minoretek**
**Winnipeg, Manitoba**

**W. Petruk**
**Core Technologies and Services Laboratory**

**November 1991**


This document is an unedited
the author of the Canada Centre
for Mineral and Energy Technology
(CANMET)
Ce document est un rapport
l'auteur du Centre canadien de
la technologie des minéraux et de
l'énergie (CANMET)

**Project: 30.90.03**
**MDA Manitoba**

12 pp

**MINERAL SCIENCES LABORATORIES**
**DIVISION REPORT MSL 91-108 (IR)**

MICROMEDIA

**Crown Copyrights Reserved**

# GRAPHIC GALENA-CLAUSTHALITE SOLID SOLUTION IN LOW-Fe SPHALERITE FROM THE TROUT LAKE MASSIVE SULFIDE ORES, FLIN FLON, MANITOBA.

RAYMOND E. HEALY[1] AND WILLIAM PETRUK[2]

[1]**Minoretek**, 219 Waterloo Street, Winnipeg, Manitoba, R3N 0S4.

[2]Mineral Processing Laboratory, **CANMET**, 555 Booth St., Ottawa, Ontario, K1A 0G1.

**ABSTRACT**

An unusual graphic intergrowth of galena-clausthalite and sphalerite observed in a single sample of Trout Lake ore was investigated. Galena-clausthalite comprises approximately 15 volume%, and a pale orange to green sphalerite the remainder of the graphic intergrowth. This Fe-poor sphalerite replaces the main deep red coloured Fe-rich sphalerite, and is associated with Sb-sulfosalts.

The average composition (in wt%) of the deep red coloured common sphalerite is 33.1% S, 58.8% Zn, 7.62% Fe and 0.13% Cd, whereas that of the pale orange to green sphalerite is 32.9% S, 64.3% Zn, 2.05% Fe and 0.34% Cd. The average composition of galena-clausthalite is 10.7% S, 6.10% Se, 83.5% Pb, corresponding to a 20% clausthalite component. The analyses indicate that late evolved pore fluids enriched in Pb, Se, Cd, Ag and Sb permeated sample TLN.1-87. The higher temperature Fe-rich sphalerite was replaced by low-Fe sphalerite with a graphic intergrowth of galena-clausthalite. The graphic texture is probably the product of co-precipitation, accommodated by the negative volume change associated with replacement of the Fe-rich sphalerite.

**INTRODUCTION**

In a comprehensive ore petrology study of the Trout Lake massive sulfide deposit (Healy & Petruk 1988) masses of graphic galena-clausthalite solid solution in low-Fe sphalerite were observed in a sample of Massive Sphalerite ore (sample TLN.1-87). Semi-quantitative electron microprobe analyses (using a MAC V at the University of Manitoba) of the galena-clausthalite gave a wide range in Se concentrations, with Se varying from <0.05 to 23 wt% (end-member clausthalite contains 27.6 wt% Se). Healy & Petruk (1989) reported that the Trout Lake ores assayed 380 ppm Pb and 49 ppm Se, and inferred that chalcopyrite, pyrite, pyrrhotite and galena (plus clausthalite) are the principal Se-bearing minerals. Subsequently, Pinard & Petruk (1989) determined that the average Se content of Trout Lake galena was 0.85 wt% Se, with values ranging from 0.1 to 3.4 wt% Se. They also found grains of galena-clausthalite solid solution with Se values up to 11.2 wt% Se.

This report presents and interprets the results of electron microprobe analyses of galena-clausthalite and sphalerite in sample TLN.1-87.

## PETROGRAPHY OF SAMPLE TLN.1-87

Sample TLN.1-87 is a sample of massive sphalerite ore consisting almost entirely of coarse-grained sphalerite with pods of quartzose and carbonate gangue. The sphalerite exhibits abundant deformational twin lamellae, and contains minor blebs and rods of pyrrhotite, but is largely free of chalcopyrite-disease. The sphalerite exhibits a deep red colour in transmitted light, which is typical of Trout Lake sphalerite and indicative of Fe-rich compositions.

The massive sphalerite contains a diffuse zone of graphic galena-clausthalite in sphalerite. The galena-clausthalite comprises approximately 15 volume% of the graphic intergrowth. The sphalerite associated with the graphic intergrowth exhibits a pale orange to green colour in transmitted light, and infills, envelopes, corrodes and replaces, and thereby postdates the main deep red coloured sphalerite (Fig. 1). These galena-clausthalite masses are associated with minor trails of chalcopyrite blebs, veinlets and grains of gudmundite, and disseminated pyrite and pyrrhotite which are partly altered to marcasite. Furthermore, several extremely coarse-grained galena-clausthalite grains that are disseminated in the ore beyond the boundary of the intergrowths contain rounded and more rarely myrmekitic inclusions of freibergite.

The galena-clausthalite exhibits textural variation; areas of (1) fine dustings (i.e., <5$\mu$m); (2) densely packed and interconnected medium-grained (i.e., 5 to 15$\mu$m) graphic blebs; (3) coarser-grained (i.e., >15$\mu$m), more discrete grains lining the boundaries of the masses and defining lineaments within the graphic sphalerite; and (4) rare, very coarse-grained (i.e., >100$\mu$m) grains irregularly disseminated beyond the masses throughout the ore. Type 3 grains probably define features such as fractures and grain boundaries within the pre-existing deep red coloured sphalerite, which may have acted as the principal conduits for the replacement process. In transmitted light, it is apparent that much of the galena-clausthalite (i.e., type 2 above) consists of zones and fringes of dendritic threads growing out from internal faces or growth zones in pale orange to green coloured sphalerite (Fig. 2A).

## METHOD OF INVESTIGATION

The chemical composition of galena-clausthalite and sphalerite in sample TLN.1-87 was investigated by electron microprobe analysis (EMPA) using the CAMECA SX-50 at the

University of Manitoba. Concentrations of S, Se, Ag, Pb and Bi in galena-clausthalite and S, Fe, Cu, Zn and Cd in sphalerite were determined by wavelength dispersive analysis (WDA). High contrast backscattered electron (BSE) imagery was used to select the analytical points on galena-clausthalite. The operating voltage and beam current were set at 20 kV and 20 nA, respectively. The counting scheme on the unknowns involved a collection time of 20 seconds on the peaks and 10 seconds on the backgrounds. Routine data reduction, including full matrix (ZAF) corrections was done with calibrated reference to stored standard intensity data generated in previous analytical runs.

## RESULTS

### Sphalerite

Ten analyses of the deep red coloured common sphalerite (sphalerite I) gave a narrow range in composition (Table 1), with an average composition (in wt%) of 33.1% S, 58.8% Zn, 7.62% Fe, 0.13% Cd and 0.03% Cu (Total = 99.7%). Fifteen analyses of the pale orange to green sphalerite (sphalerite II) also gave a narrow range in composition (Table 2), with an average composition (in wt%) of 32.9% S, 64.3% Zn, 2.05% Fe, 0.34% Cd and 0.11% Cu (Total = 99.7%). The Cd values indicate a significant increase in Cd with increased Zn and decreased Fe in sphalerite II.

### Galena-Clausthalite Solid Solution

Twenty five analyses of galena-clausthalite gave a large range in composition (Table 3), with an average composition (in wt%) of 10.7% S, 6.10% Se, 83.5% Pb and 0.01% Ag (Total = 100.3%), corresponding to a 20% clausthalite component. Because of poor counting statistics, the Ag values are statistically not significantly different form zero, and are not considered further. Bi was undetected. The distribution of Se seems to be trimodal with peaks at approximately 1 to 2 wt%, 5 wt% and 22 wt% Se (Fig. 3). The peak at approximately 22 wt% Se corresponds to 4 analyses on two grains lining the boundary of the masses (i.e., type 3). It is apparent that inhomogeneity within grains is less than between grains, and that equilibration has not been achieved.

## DISCUSSION

The higher Cd concentration in pale orange to green sphalerite II suggests (1) that sphalerite II did not replace, but grew on, and enveloped sphalerite I, or (2) that

sphalerite II is replacive, but that additional Cd was metasomatically introduced during the replacement of sphalerite I. The latter is favoured as sphalerite II crosscuts and corrodes sphalerite I, which occasionally persists as rounded relict islands in sphalerite II (See Figure 2B). The 3-fold increase in the Cd concentration of sphalerite II cannot be accounted for by mass balance considerations of the relative volumes of sphalerite I. The reaction that replaces sphalerite I containing 87 mole% ZnS and 13 mole% FeS, with sphalerite II containing 96 mole% ZnS and 4 mole% FeS can be expressed as

$$100\ (Zn_{0.87}Fe_{0.13})S \longrightarrow 90\ (Zn_{0.96}Fe_{0.04})S + 10\ FeS$$

This reaction results in a 10 volume% loss of sphalerite, and is isochemical with respect to ZnS, but evolves 10 mole% FeS. However, as the graphic galena-clausthalite comprises 15% of the intergrowth, and assuming identical molar volumes for sphalerite I and II, both FeS and ZnS are evolved according to the reaction

$$100\ (Zn_{0.87}Fe_{0.13})S \longrightarrow 85\ (Zn_{0.96}Fe_{0.04})S + 10\ FeS + 5\ ZnS$$

Thus, both Fe and Zn are evolved with much of the excess Fe probably precipitated as the associated gudmundite, pyrite and marcasite. Minor incipient replacement of sphalerite I by sphalerite II is observed irregularly distributed throughout the sample as diffuse apparently opaque (in transmitted light) patches in sphalerite I. The opaque character is produced by the dispersion of light on pits and voids in sphalerite I, which are not infilled by galena-clausthalite.

In their study of the PbS-PbSe system, Wright et al. (1965) found that metastable compositions with excess Se above the bulk composition of the starting material persisted even at higher temperatures, indicating extremely low rates of compositional equilibration. Thus, the wide range in composition does not necessarily indicate growth at extremely low temperatures, where equilibration would be kinetically constrained, nor do high Se/S ratios necessarily reflect equivalently high Se/S activity ratios in the pore fluid. Czamanske & Hall (1975) propose that the Se concentrations of galena-clausthalite solid solution and other phases in the 'late sulfosalt mineralization' at the Darwin mine, simply reflect the availability of Se during late Ag, Bi and Se enrichment. The association of minor freibergite and gudmundite with galena-clausthalite is consistent with this late enrichment of Ag, Sb and Se, but not Bi in sample TLN.1-87. Bi is conspicuously absent either as distinct Bi-minerals or as a substituent element in any of the associated phases.

The above discussion suggests that late evolved pore fluids enriched in Pb, Se, Cd, Ag and Sb permeated the massive sphalerite of sample TLN.1-87 along an irregular zone. The earlier Fe-rich sphalerite I, equilibrated at higher temperatures, was replaced by low-Fe sphalerite II with a graphic intergrowth of galena-clausthalite solid solution. The graphic texture is probably the product of simple co-precipitation, accommodated by the negative volume change from sphalerite I to sphalerite II. The lower Fe content of sphalerite II is consistent with equilibration at higher activities of $S_2$ and/or more probably lower temperature.

**REFERENCES**


**Czamanske, G.K. & Hall, W.E. (1975):** The Ag-Bi-Pb-Sb-S-Se-Te mineralogy of the Darwin lead-silver-zinc deposit, southern California. **Econ. Geol.** 70, 1092-1110.

**Healy, R.E. & Petruk, W. (1988):** The mineral characteristics that affect metal recoveries from Cu, Zn, Pb and Ag ores in Manitoba. Part I, An investigation of the ore mineralogy of the Trout Lake deposit. CANMET, Dept. Energy, Mines & Resources, Ottawa, Canada, Mineral Sciences Laboratory, Investigation Report **MRP/MSL 88-61(IR).**

_____**&**_____ **(1989):** The mineral characteristics that affect metal recoveries from Cu, Zn, Pb and Ag ores in Manitoba. **Part II**, A mineralogical evaluation of the behaviour of metallic minerals in the Trout Lake concentrator circuit. CANMET, Dept. Energy, Mines & Resources, Ottawa, Canada, Mineral Sciences Laboratory, Investigation Report, **MRP/MSL 89-87(IR).**

**Pinard, R.G. & Petruk, W. (1989):** Silver content of galena from Trout Lake deposit in Flin Flon. CANMET, Dept. Energy, Mines & Resources, Ottawa, Canada, Mineral Sciences Laboratory, Process Mineralogy Section Report **M-4070.**

**Wright, H.D., Barnard, W.M. & Halbig, J.B. (1965):** Solid solution in the systems ZnS-ZnSe and PbS-PbSe at 300°C. and above. **Amer. Mineral.** 50, 1802-1815.

**TABLE 1. CHEMICAL COMPOSITION (MICROPROBE DATA) OF SPHALERITE I.**

| Anal | Wt% | | | | | | At% | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Zn | S | Fe | Cd | Cu | Total | Zn | S | Fe | Cd | Cu |
| 1 | 58.7 | 33.0 | 7.88 | 0.06 | 0.03 | 99.6 | 43.4 | 49.7 | 6.82 | 0.03 | 0.02 |
| 2 | 58.6 | 33.0 | 7.90 | 0.17 | 0.01 | 99.7 | 43.4 | 49.7 | 6.84 | 0.07 | 0.00 |
| 3 | 58.0 | 33.3 | 7.78 | 0.16 | 0.05 | 99.2 | 42.9 | 50.2 | 6.74 | 0.07 | 0.04 |
| 4 | 58.6 | 32.9 | 7.91 | 0.14 | 0.04 | 99.6 | 43.4 | 49.6 | 6.86 | 0.06 | 0.03 |
| 5 | 59.0 | 33.0 | 7.88 | 0.21 | 0.05 | 100.4 | 43.3 | 49.8 | 6.77 | 0.09 | 0.04 |
| 6 | 59.1 | 33.2 | 7.42 | 0.14 | 0.02 | 99.9 | 43.6 | 49.9 | 6.41 | 0.06 | 0.01 |
| 7 | 59.0 | 33.2 | 7.77 | 0.08 | 0.04 | 100.1 | 43.4 | 49.8 | 6.69 | 0.03 | 0.03 |
| 8 | 58.8 | 33.5 | 7.54 | 0.18 | 0.01 | 100.1 | 43.2 | 50.2 | 6.48 | 0.08 | 0.01 |
| 9 | 59.2 | 33.4 | 7.87 | 0.08 | 0.03 | 100.6 | 43.3 | 49.9 | 6.74 | 0.04 | 0.02 |
| 10 | 59.0 | 32.8 | 6.29 | 0.12 | 0.01 | 98.2 | 44.3 | 50.1 | 5.53 | 0.05 | 0.01 |
| **Mean** | 58.8 | 33.1 | 7.62 | 0.13 | 0.03 | 99.7 | 43.4 | 49.9 | 6.59 | 0.06 | 0.02 |
| σ | 0.35 | 0.24 | 0.50 | 0.05 | 0.02 | 0.66 | 0.35 | 0.21 | 0.40 | 0.02 | 0.01 |

**TABLE 2. CHEMICAL COMPOSITION (MICROPROBE DATA) OF SPHALERITE II.**

| Anal | Wt% | | | | | | At% | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Zn | S | Fe | Cd | Cu | Total | Zn | S | Fe | Cd | Cu |
| 1 | 64.4 | 32.9 | 1.78 | 0.36 | 0.09 | 99.5 | 48.1 | 50.1 | 1.55 | 0.16 | 0.07 |
| 2 | 65.0 | 33.3 | 2.10 | 0.35 | 0.05 | 100.8 | 47.9 | 50.1 | 1.81 | 0.15 | 0.04 |
| 3 | 63.2 | 32.7 | 2.72 | 0.46 | 0.02 | 99.1 | 47.4 | 50.0 | 2.39 | 0.20 | 0.02 |
| 4 | 64.7 | 32.9 | 2.32 | 0.47 | 0.01 | 100.4 | 48.0 | 49.8 | 2.02 | 0.20 | 0.01 |
| 5 | 64.7 | 32.9 | 2.05 | 0.36 | 0.05 | 100.1 | 48.1 | 49.9 | 1.78 | 0.15 | 0.03 |
| 6 | 64.7 | 32.6 | 1.92 | 0.36 | 0.12 | 99.7 | 48.4 | 49.7 | 1.68 | 0.16 | 0.09 |
| 7 | 64.4 | 32.9 | 1.75 | 0.34 | 0.04 | 99.4 | 48.2 | 50.1 | 1.53 | 0.15 | 0.03 |
| 8 | 63.4 | 32.9 | 2.65 | 0.46 | 0.09 | 99.5 | 47.3 | 50.1 | 2.32 | 0.20 | 0.07 |
| 9 | 62.6 | 32.7 | 2.70 | 0.33 | 0.13 | 98.5 | 47.1 | 50.2 | 2.38 | 0.14 | 0.10 |
| 10 | 64.8 | 32.9 | 1.72 | 0.29 | 0.13 | 99.8 | 48.3 | 50.0 | 1.50 | 0.12 | 0.10 |
| 11 | 65.3 | 32.8 | 1.16 | 0.25 | 0.24 | 99.7 | 48.8 | 49.9 | 1.02 | 0.11 | 0.18 |
| 12 | 63.4 | 32.4 | 1.76 | 0.19 | 0.41 | 98.1 | 48.0 | 50.0 | 1.56 | 0.08 | 0.32 |
| 13 | 64.2 | 33.1 | 2.19 | 0.30 | 0.12 | 99.9 | 47.7 | 50.2 | 1.91 | 0.13 | 0.09 |
| 14 | 64.6 | 33.0 | 1.85 | 0.22 | 0.07 | 99.8 | 48.1 | 50.2 | 1.611 | 0.10 | 0.05 |
| 15 | 64.9 | 33.5 | 2.04 | 0.30 | 0.07 | 100.8 | 47.8 | 50.3 | 1.76 | 0.13 | 0.05 |
| **Mean** | 64.3 | 32.9 | 2.05 | 0.34 | 0.11 | 99.7 | 48.0 | 50.0 | 1.79 | 0.15 | 0.08 |
| σ | 0.77 | 0.27 | 0.43 | 0.08 | 0.10 | 0.74 | 0.44 | 0.17 | 0.37 | 0.04 | 0.08 |

**TABLE 3. CHEMICAL COMPOSITION (MICROPROBE DATA) OF GALENA-CLAUSTHALITE.**

| Anal | Wt% | | | | | At% | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Pb | Ag | S | Se | Total | Pb | Ag | S | Se |
| 1 | 85.9 | 0.00 | 13.1 | 1.37 | 100.3 | 49.4 | 0.00 | 48.6 | 2.07 |
| 2 | 83.4 | 0.02 | 10.6 | 6.36 | 100.4 | 49.5 | 0.02 | 40.6 | 9.90 |
| 3 | 83.5 | 0.00 | 10.7 | 6.40 | 100.6 | 49.4 | 0.00 | 40.7 | 9.92 |
| 4 | 82.6 | 0.18 | 10.1 | 7.51 | 100.4 | 49.2 | 0.20 | 38.8 | 11.8 |
| 5 | 82.7 | 0.00 | 10.5 | 6.77 | 99.9 | 49.2 | 0.00 | 40.3 | 10.6 |
| 6 | 83.3 | 0.03 | 10.6 | 6.46 | 100.4 | 49.3 | 0.03 | 40.6 | 10.0 |
| 7 | 74.5 | 0.00 | 2.18 | 22.9 | 99.6 | 50.1 | 0.00 | 9.47 | 40.5 |
| 8 | 76.6 | 0.00 | 4.42 | 18.4 | 99.4 | 50.0 | 0.00 | 18.6 | 31.4 |
| 9 | 73.9 | 0.00 | 2.90 | 21.0 | 97.8 | 50.0 | 0.00 | 12.7 | 37.3 |
| 10 | 85.3 | 0.00 | 13.1 | 1.24 | 99.5 | 49.3 | 0.00 | 48.8 | 1.89 |
| 11 | 85.3 | 0.00 | 11.6 | 4.53 | 101.4 | 49.5 | 0.00 | 43.6 | 6.90 |
| 12 | 84.8 | 0.00 | 11.8 | 3.74 | 100.4 | 49.6 | 0.00 | 44.7 | 5.74 |
| 13 | 85.3 | 0.10 | 11.6 | 4.56 | 101.6 | 49.4 | 0.11 | 43.6 | 6.93 |
| 14 | 82.6 | 0.04 | 11.5 | 4.94 | 99.0 | 48.7 | 0.05 | 43.7 | 7.64 |
| 15 | 84.7 | 0.00 | 11.4 | 4.86 | 100.9 | 49.6 | 0.00 | 42.9 | 7.46 |
| 16 | 84.6 | 0.00 | 11.0 | 5.45 | 101.0 | 49.9 | 0.00 | 41.7 | 8.42 |
| 17 | 74.9 | 0.13 | 2.11 | 23.1 | 100.2 | 50.2 | 0.16 | 9.14 | 40.5 |
| 18 | 85.8 | 0.00 | 13.2 | 1.21 | 100.2 | 49.4 | 0.00 | 48.8 | 1.82 |
| 19 | 84.4 | 0.00 | 11.2 | 4.56 | 100.2 | 50.0 | 0.00 | 43.0 | 7.10 |
| 20 | 84.8 | 0.00 | 11.5 | 4.27 | 100.6 | 49.7 | 0.00 | 43.7 | 6.57 |
| 21 | 85.0 | 0.00 | 11.5 | 4.49 | 100.9 | 49.8 | 0.00 | 43.3 | 6.89 |
| 22 | 84.4 | 0.00 | 11.5 | 4.42 | 100.2 | 49.5 | 0.00 | 43.7 | 6.81 |
| 23 | 85.2 | 0.00 | 11.6 | 4.63 | 101.4 | 49.5 | 0.00 | 43.4 | 7.07 |
| 24 | 85.1 | 0.00 | 11.6 | 4.26 | 101.0 | 49.7 | 0.00 | 43.8 | 6.52 |
| 25 | 85.9 | 0.00 | 13.1 | 1.21 | 100.2 | 49.4 | 0.00 | 48.8 | 1.82 |
| 26 | 85.9 | 0.00 | 13.0 | 1.29 | 100.2 | 49.6 | 0.00 | 48.5 | 1.95 |
| 27 | 86.5 | 0.00 | 13.4 | 0.59 | 100.5 | 49.5 | 0.00 | 49.6 | 0.89 |
| 28 | 85.1 | 0.00 | 12.7 | 2.13 | 100.0 | 49.3 | 0.00 | 47.5 | 3.24 |
| 29 | 86.5 | 0.00 | 12.6 | 2.14 | 101.2 | 49.9 | 0.00 | 46.8 | 3.24 |
| 30 | 86.0 | 0.00 | 12.7 | 2.20 | 100.9 | 49.5 | 0.00 | 47.1 | 3.33 |
| 31 | 85.1 | 0.01 | 12.5 | 2.18 | 99.9 | 49.5 | 0.01 | 47.1 | 3.33 |
| **Mean** | 81.2 | 0.02 | 8.80 | 9.84 | 99.8 | 49.5 | 0.03 | 33.9 | 16.5 |
| $\sigma$ | 4.43 | 0.06 | 4.06 | 7.92 | 0.82 | 0.35 | 0.06 | 14.6 | 14.3 |

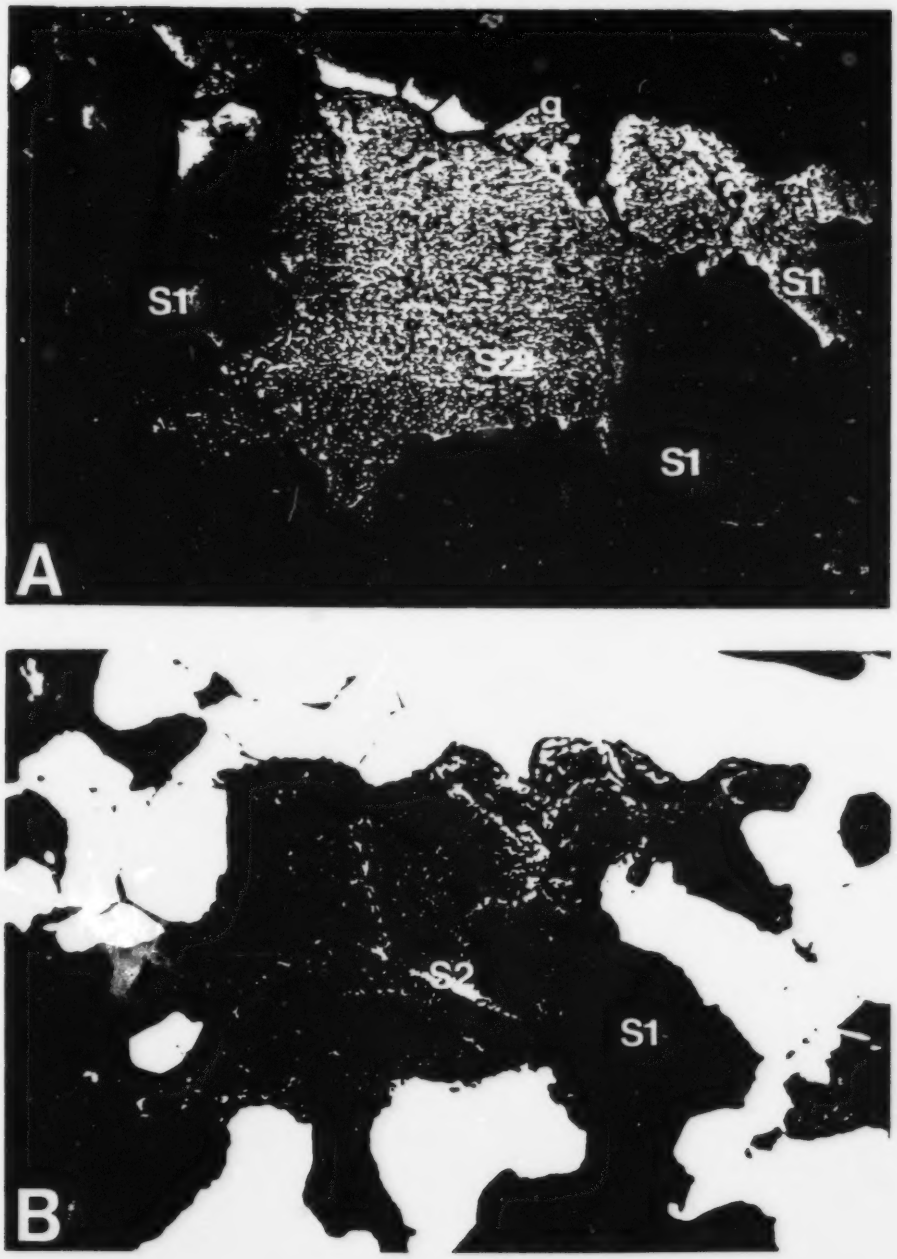



**Figure 1. (A)** Mass of graphic galena-clausthalite in sphalerite II replacing sphalerite I. Note the veinlet of gudmundite at 'g' and type 3 galena-clausthalite at 'x'. Reflected Light. Mag. = x115. **(B)** Transmitted light view of A, showing sphalerite I (grey) and sphalerite II (light grey) hosting the densely intergrown opaque galena-clausthalite (black). Mag. = x115.

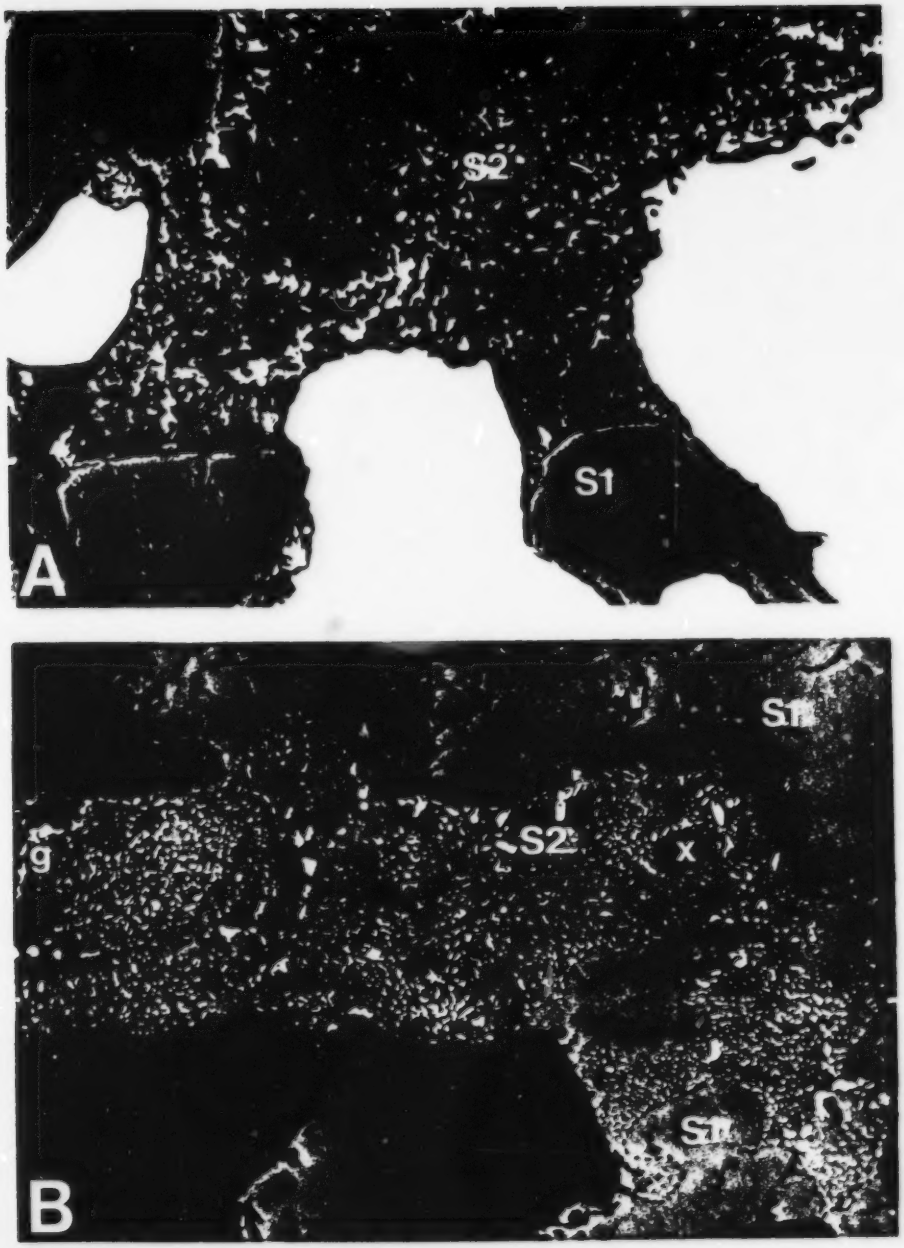



**Figure 2. (A)** Detail of lower left quadrant of Figure 1B, showing threads of graphic galena-clausthalite in sphalerite II. Note sphalerite II corrodes and envelopes sphalerite I. Transmitted Light. Mag. = x390. **(B)** Mass of graphic galena-clausthalite in sphalerite II, which has replaced and corroded sphalerite I, though the latter persists as rounded relict islands e.g., at 'x'. Note veinlet of gudmundite at 'g', and type 3 galena-clausthalite defining lineaments within, and the boundaries of the mass. Reflected Light. Mag. = x115.

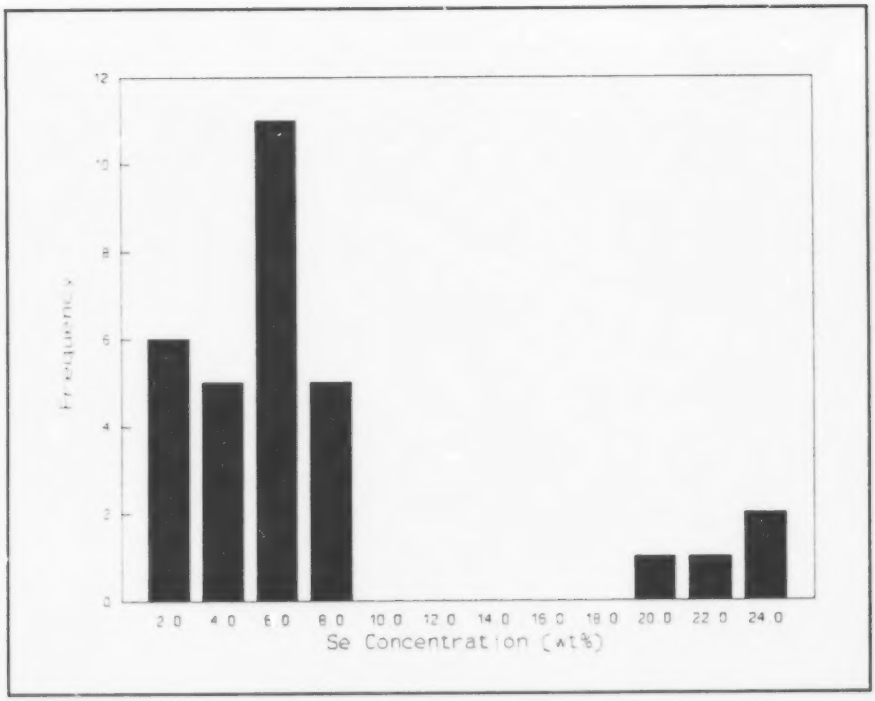



**Figure 3.** Distribution of Se in galena-clausthalite solid solution from sample TLN.1-87. Distribution based on compositions from 31 microprobe analyses (Table 3).